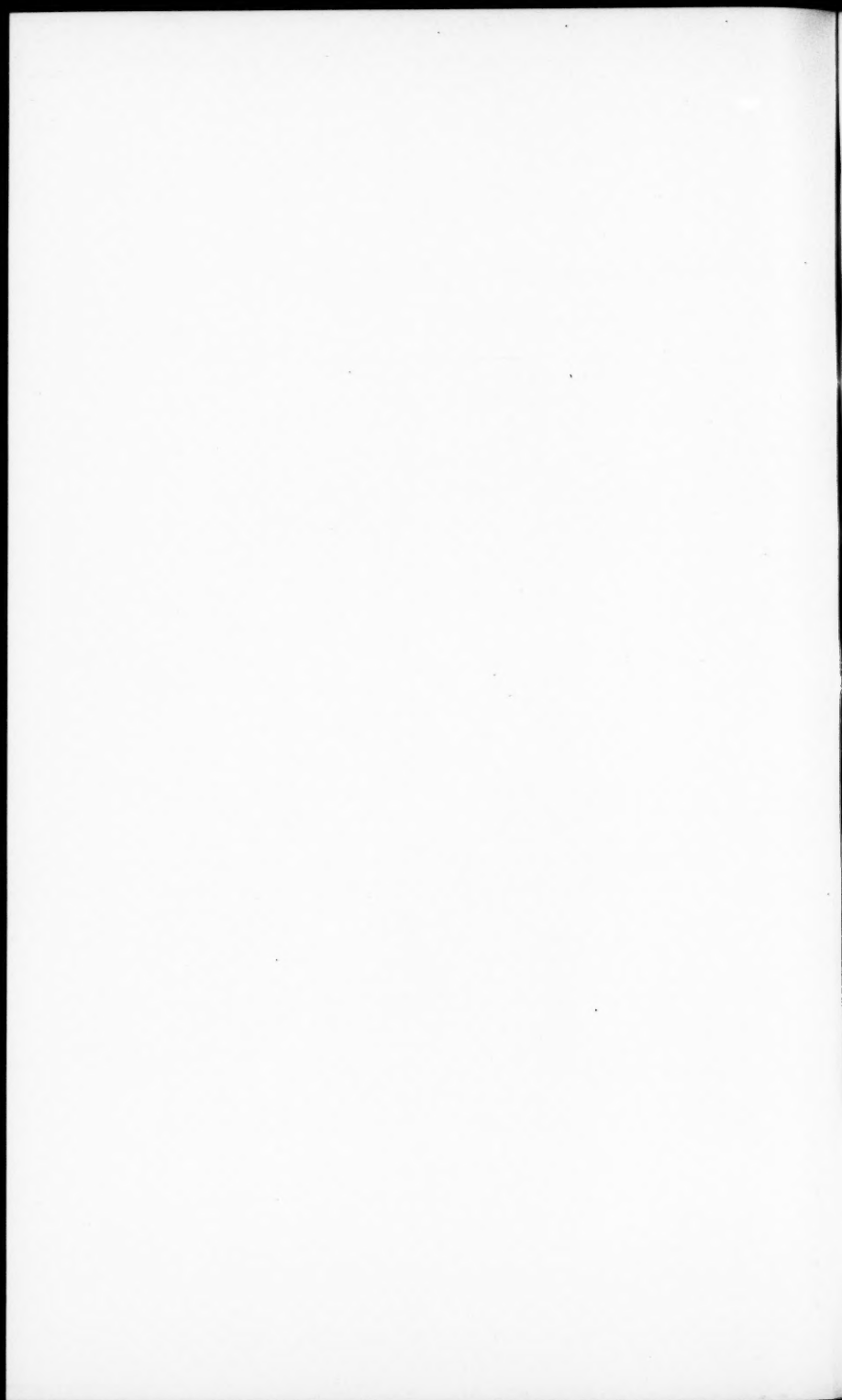


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THE COMPRESSIBILITY AND PRESSURE COEFFICIENT OF
RESISTANCE OF TEN ELEMENTS.

By P. W. BRIDGMAN.



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INTRODUCTION.

The data to be presented in this paper were obtained in continuation of the program of measuring the two properties above for all the elements available.¹ The range of these measurements is the same as that of the previous work, 0 to 12000 kg/cm², and 30° and 75° C, in most cases. The methods of measurement were also the same, so that no new discussion of them is needed. The compressibilities were all measured in the so-called "lever piezometer for small specimens." The measurements on Pr, La, Be, and Ce were made with the identical apparatus that was used in the previous measurements. Damage to the high resistance wire attached to the lever necessitated its replacement for the other substances. After this replacement the lever apparatus was recalibrated as previously described, both by measuring the magnification with a micrometer, and by measuring the apparent compressibility of pure iron at 30° and 75°. The constants of the apparatus were found to have changed only a few tenths of a per cent.

NUMERICAL DATA.

Praseodymium. I owe this metal to the kindness of Dr. H. C. Kremers, of the University of Illinois, who has long specialized in the preparation of the rare metals. The metal used in my measurements was some of the identical metal, the preparation and the properties of which have been described by Kremers.² The salts from which the metal was electrolyzed had a purity of 99.7%; the only known impurities being 0.02% Nd, and 0.01% La. Kremers states that the metal formed by electrolysis, which took place in a graphite crucible, was doubtless of high purity, but no special analysis was made to find exactly what the purity was. It is evident that there could have been no appreciable impurity of other rare metals, but it does not seem impossible that some of the more common impurities may have been absorbed from the crucible. The metal as furnished to me was in the form of small slugs, about 6 mm. in diameter, sealed into glass under oil. I formed the specimens for my measurements by extrusion of these slugs at a bright red heat through dies of Cr-Va steel, in an atmosphere of nitrogen. The compressibility sample was 3 mm. in diameter, and 1.3 cm. long. The extruded wire for the resistance measurements was 0.085 cm. in diameter, and about 15 cm. long. This metal extrudes to wire very easily under the proper conditions, and pieces were obtained much longer than necessary for these measurements. This wire has high mechanical strength, and in superficial appearance is much like soft iron wire.

Compressibility. This was measured in the regular way at 30° and 75°. The crystal system of Pr has apparently not yet been determined. Assuming that the compressibility of my sample is the same in every direction, which is probably not far from the truth because of the method of formation by extrusion, even if it should prove not to be cubic, the following results were computed from the measured linear compressibility:

$$\text{At } 30^\circ \quad \frac{\Delta V}{V_0} = -33.8 \times 10^{-7}p + 13. \times 10^{-12}p^2.$$

$$\text{At } 75^\circ \quad \frac{\Delta V}{V_0} = -34.6 \times 10^{-7}p + 13. \times 10^{-12}p^2.$$

The mean arithmetical deviation of a single reading from a smooth curve was 0.55% at 30°, making two discards, and also 0.55% at 75°, with one discard. The scattering of the readings was such that no great accuracy can be attached to the second degree term; it was

certain, however, that the compressibility decreases with rising pressure, as is normal.

Electrical Resistance. This was measured with a potentiometer in the regular way. Contacts were made with spring clips, since it is not possible to solder this metal, taking pains that the contacts should be at only a single well defined point. The resistance decreases with pressure, as is normal, and within the limits of error, the decrease is linear. The mean coefficients to 12000 kg. were:

$$\text{At } 30^{\circ}, - 3.1 \times 10^{-7}$$

$$\text{At } 75^{\circ}, - 8.3 \times 10^{-7}$$

At 30° the mean deviation of a single reading from a smooth curve was 6.0%, and at 75° , 2.4% of the maximum effect. The pressure coefficients are seen to be unusually low, which accounts for the unusually large scattering of the individual readings. The very large change of the pressure coefficient with temperature is most unusual.

In addition to the pressure effect, the specific resistance at 30° was found to be 6.9×10^{-5} , and the temperature coefficient at 0° 0.00165. This last value is so low that it would seem probable that a rather large amount of impurity must have been absorbed during the electrolysis. Presumably this may have been gaseous in character; Kremers states that gases are easily absorbed.

By combining the values above for the pressure and the temperature coefficients, it will be found that the temperature coefficient at 12000 kg. is about 10% less than at atmospheric pressure.

Lanthanum. This I also owe to the kindness of Dr. Kremers. The methods of preparation have been described by him.³ He states that the metal is free from other metals. He found it to melt sharply at 826° , which is much higher than the previously accepted value for the melting point, 810° , and therefore evidence of high purity. The samples on which my measurements were made were formed by extrusion, and were of approximately the same dimensions as those of Pr. La extrudes somewhat more readily than Pr, and at a somewhat lower temperature. Its mechanical properties are not markedly different.

Compressibility. The compressibility measurements went perfectly smoothly, without incident of any kind. Assuming that the sample was equally compressible in all directions (the crystal system of La seems not to have been yet determined), the following results

were found for the cubic compressibility from the measured linear compressibility:

$$\text{At } 30^{\circ} \quad \frac{\Delta V}{V_0} = -35.13 \times 10^{-7}p + 14.7 \times 10^{-12}p^2.$$

$$\text{At } 75^{\circ} \quad \frac{\Delta V}{V_0} = -35.01 \times 10^{-7}p + 17.1 \times 10^{-12}p^2.$$

The average deviation of a single reading from a smooth curve was 0.45% at 30° and 0.42% at 75°.

The temperature coefficient of compressibility of La is abnormal in that it is negative; this effect seems larger than possible experimental error.

Resistance. The resistance was measured at 30° and 75°. The pressure coefficient is negative, as is normal. At 30°, the relation between pressure and resistance was linear within experimental error, the average deviation of a single reading from a straight line being 0.84% of the maximum change. At 75° the relation was obviously not linear within experimental error, but could be represented by a second degree equation with curvature in the normal direction. The average deviation from a smooth curve of a single reading at 75° was 0.54% of the maximum change. The results follow:

$$\text{At } 30^{\circ} \quad \frac{\Delta R}{R(1 \text{ kg}, 30^{\circ})} = -1.199 \times 10^{-6}p.$$

$$\text{At } 75^{\circ} \quad \frac{\Delta R}{R(1 \text{ kg}, 75^{\circ})} = -1.810 \times 10^{-6}p + 9.7 \times 10^{-12}p^2.$$

Again, as in the case of Pr, the temperature coefficient of the pressure coefficient is unusually large.

The absolute specific resistance of this sample was found to be 5.76×10^{-5} at 0°. The temperature coefficient of resistance at atmospheric pressure at 0° is 0.00213, reduced from readings at 20° and 75°, assuming a linear relation between temperature and resistance.

The pressure coefficient of resistance of another sample of La has been measured by me.⁴ This sample had a temperature coefficient of 0.00148, considerably lower than that above, so that presumably the previous sample was less pure. The pressure coefficient of the previous sample was, on the other hand, about twice as great as that of the new sample, being -3.9×10^{-6} , independent of temperature.

This is unusual; the pressure coefficient of the purer metal is usually greater numerically than that of the less pure metal, although the difference is not usually so pronounced as for the temperature coefficient.

Cerium. This metal I again owe to the kindness of Dr. Kremers, who has described the method of preparation and its properties.⁵ The specimens were prepared for my measurements by extrusion in the same way as Pr and La. The extrusion temperature is lower, and the extrusion easier than for the other two metals. I have previously measured the compressibility of Ce⁶, but on a sample whose temperature coefficient of resistance was so low, 0.001, that it did not seem worth while measuring the pressure coefficient of resistance, in view of the presumptively high impurity. The point in now repeating the measurements is that this sample is presumably of much higher purity; Kremers states that the method of preparation is such that the metal should be free from iron, which is known to be present in nearly all the Ce that has hitherto been available.

This pure Ce was found to be polymorphic at high pressures, a phenomenon of which no trace whatever was shown by the impurer sample. A transition at high pressures was first found during the compressibility measurements, and was shown by large irregularities at the upper end of the curve, and was verified on taking the apparatus apart by distortion and permanent changes of dimensions of the specimen. The existence of the transition was later verified by measurements of the electrical resistance. These measurements gave fairly good coordinates for the transition, which was found to take place at 7600 kg. at 30° and 9400 at 75°. The transition is slow and not perfectly sharp; perhaps if the metal were perfectly pure the transition would be found to be sharp. Unfortunately, there was not enough of the metal available to determine the volume change at the transition, or the other thermal parameters.

Compressibility. After the transition was found during the first attempted compressibility measurements, the sample was annealed by heating for six hours to a nearly red heat in a sealed glass tube. After annealing, the compressibility was determined, the pressure being restricted to a range of 4000 kg., in order to avoid all possible effects of the transition. It was not possible to determine the compressibility of the high pressure modification without changing the apparatus. The following results were found for the volume compressibility, assuming equal compressibility in all directions:

$$\text{At } 30^\circ \quad \frac{\Delta V}{V_0} = -45.63 \times 10^{-7} p - 161.4 \times 10^{-12} p^2.$$

$$\text{At } 75^\circ \quad \frac{\Delta V}{V_0} = -45.03 \times 10^{-7} p - 151.5 \times 10^{-12} p^2.$$

The average deviation of a single reading from a smooth curve was 0.51% at 30° and 0.54% at 75°.

These results for the compressibility of Ce are highly anomalous in two respects. In the first place, the temperature coefficient of compressibility is negative, in both the first and the second degree terms. Secondly, the direction of curvature is abnormal, in that the compressibility becomes greater at high pressures. This is the first pure substance in which this phenomenon has been found, the only previously known examples are some of the glasses with high SiO₂ content.⁷ It is natural to see some connection between the anomalous effect here and the existence of a second modification. It will be noticed that both these anomalies are much too large to be accounted for by any possible experimental error.

The compressibility of this pure Ce is very much higher than that previously found for impure Ce, 35.74×10^{-7} at 30°. The difference is in a direction to be accounted for by a large impurity of iron in the first sample. The temperature coefficient and curvature of the impure Ce were both normal.

Resistance. The resistance phenomena under pressure are no less surprising than the compressibility phenomena. The low pressure modification is abnormal in that the resistance increases with pressure. The pressure coefficient of resistance of the low pressure modification was determined on a virgin sample, which had never experienced the transition. Within experimental error, the relation between pressure and resistance was linear at both 30° and 75°. The following results were found:

$$\text{At } 30^\circ \quad \frac{\Delta R}{R(1 \text{ kg}, 30^\circ)} = +4.42 \times 10^{-6} p, \quad \text{range } 3000 \text{ kg.}$$

$$\text{At } 75^\circ \quad \frac{\Delta R}{R(1 \text{ kg}, 75^\circ)} = +2.77 \times 10^{-6} p, \quad \text{range } 6000 \text{ kg.}$$

The average deviation of a single reading from a smooth curve was 0.7% of the maximum effect at 30°, and at 75°, 1.6%.

The high pressure modification is normal in that the resistance decreases with rising pressure. Within the limits of experimental

error, which might perhaps have been as high as 10%, the relation between pressure and ΔR is linear between 9000 and 12000 kg. at 30°, and the pressure coefficient is -1.42×10^{-5} , in terms of the resistance at 9000 kg. This is also the coefficient, within somewhat larger limits of error, at 75°. It was not possible to compare the specific resistances of the two modifications, because of the unknown difference of dimensions.

The specific resistance of the low pressure modification at 30° was 7.48×10^{-5} . The temperature coefficient, reduced to 0° from readings at 19° and 75°, assuming linearity, was 0.00097. This is surprisingly low, lower even than found for the previous sample, which was known to be impure with iron. All the chemical evidence, as well as the fact that a transition has been found, points to the high purity of this sample. It is evident enough that the low pressure modification is highly anomalous. It may be that in addition to its other anomalies, we have here the first known example of a pure metal with a temperature coefficient of resistance very much less than 1/t.

Beryllium. My particular interest in this metal was my expectation that it would be found to be one of the comparatively few metals with a positive pressure coefficient of resistance. The reason for this expectation was its proximity to Li at the left in the periodic table and to Ca and Sr below, all of which have positive coefficients. This expectation did not turn out to be correct.

Beryllium was obtained from two sources. The first I owe to the kindness of Professor A. Stock of Berlin, who sent me a nugget of beryllium prepared by electrolysis of the fused salts, the linear dimensions of which varied from 1 to 2 cm. The compressibility was determined on a sample of this, and I spent much time trying to get from it a sample suitable for the resistance measurements. Beryllium is very hard, and can be worked only by grinding. The interior of the piece unfortunately proved to have many inclusions of the original fused salt, so that it was not possible to grind from it a straight piece of sufficient length. I found that Be becomes soft when hot, and a pellet may be squeezed flat at a red heat between cold steel plates. This led to the attempt to extrude it hot, but unsuccessfully. I used Cr-Va steel dies, and also dies of a high speed steel, specially recommended for hot work, but at no temperature between a dull red and a bright yellow did the Be become softer than the steel, but the die was always deformed before extrusion started. An attempt to cast a slender rod in a vacuum electric

furnace was also unsuccessful. I was finally fortunate enough to obtain a rod of cast Be, 4.6 mm. in diameter and 9 cm. long, made in this country by Dr. H. S. Cooper of the Kemet Laboratories, and I take this occasion to express my indebtedness. This rod was apparently entirely free from inclusions of any kind. It was rather larger than would have been desirable to give the best results for the change of resistance, but nevertheless the accuracy was high enough to leave absolutely no doubt as to the general character of the results.

Compressibility. The compressibility was measured, as usual, at 30° and 75°, with the following results, assuming equal compressibility in all directions. Be is known to be hexagonal, but the crystal-line structure of this casting was very fine, so that the measured linear compressibility along the length of the rod doubtless gave a fair average of the linear compressibility in all directions.

$$\text{At } 30^\circ \text{ and } 75^\circ, \quad \frac{\Delta V}{V_0} = -8.55 \times 10^{-7}p + 3.88 \times 10^{-12}p^2.$$

Within experimental error, no difference could be found between the compressibility at 30° and 75°. The average deviation of a single reading from a smooth curve was 0.12% at 30° (two discards out of 13 observations) and 0.17% at 75° (three discards out of 14 observations). The compressibility of the German sample was 9.0×10^{-7} ; this is somewhat higher than the other, as is to be expected because of the effect of the inclusions.

Resistance. The resistance of only the sample from Dr. Cooper was measured. This was determined with the potentiometer in the regular way, with four terminals. Connections were made by turning in the lathe with a diamond point four grooves of *V* section, two near each end of the rod, and snapping around the grooves a very fine helical spring. The resistance decreases under pressure, which is normal for the majority of metals. The results were accurate enough to establish that the curvature is also in the normal direction. The results were as follows:

$$\text{At } 30^\circ \quad \frac{\Delta R}{R(1 \text{ kg}, 30^\circ)} = -1.11 \times 10^{-6}p + 1.2 \times 10^{-11}p^2.$$

$$\text{At } 75^\circ \quad \frac{\Delta R}{R(1 \text{ kg}, 75^\circ)} = -1.58 \times 10^{-6}p + 2.6 \times 10^{-11}p^2.$$

At 30° the average deviation from a smooth curve of a single reading

was 3.3% (13 readings with no discards), and at 75° was 3.4% (14 readings, with no discards).

The specific resistance at 30° was 10.6×10^{-6} . The temperature coefficient at 0°, reduced from readings at 30° and 75°, assuming linearity, was 0.00328. This suggests fairly high purity.

The density at room temperature, 20° \pm , was found to be 1.820.

Barium. I owe this metal to the kindness of Dr. A. J. King of Syracuse University, who prepared it by the method of P. S. Danner.⁸ Professor Saunders was kind enough to make a spectroscopic analysis, which showed only a trace of Sr. The spectroscopic examination was made with a quartz spectrograph, over a wide spectral range. Professor Saunders characterizes the Ba as "extraordinarily pure."

Two specimens were provided by Dr. King. One had been melted in an iron vessel to a coherent slug, and was furnished to me sealed into glass under oil. The other had not been melted since electrolysis, and was sealed into glass in an atmosphere of argon. This was presumably the purer of the two. The compressibility sample was taken from the first sample, the second not being large enough, and the resistance sample from the second. The specimens were formed by cold extrusion under oil through a steel die; this could be done very easily.

Compressibility. The measurements went smoothly, without incident. The following are the results, assuming equal compressibility in all directions. (The crystalline system has apparently not yet been determined).

$$\text{At } 30^\circ \quad \frac{\Delta V}{V_0} = -101.9 \times 10^{-7}p + 129 \times 10^{-12}p^2.$$

$$\text{At } 75^\circ \quad \frac{\Delta V}{V_0} = -106.3 \times 10^{-7}p + 149 \times 10^{-12}p^2.$$

The average deviation of a single reading from a smooth curve was 0.53% at 30°, and 0.56% at 75°. The results are represented above by a second degree curve, but it is probable that a strict regard for the magnitude of the experimental error would have justified the inclusion of another term. This extra term, if it had been given, would have been abnormal, in that the maximum deviation from linearity occurred at both temperatures at pressures somewhat higher than 6000, instead of exactly at 6000, as is the case with a second degree curve, or at less than 6000, as for all other substances

so far studied whose compressibility could not be represented by a second degree curve, as for example the alkali metals.

Resistance. The resistance measurements were made with the potentiometer in the regular way. The sample was about 0.07 cm. in diameter and 15 cm. long. Current and potential connections were made near each end with springs resting in notches cut across the wire in such a way as to prevent motion. The results were not at all what was expected. A high positive pressure coefficient was expected, by analogy with Ca and Sr. Instead, the initial effect is negative, as is normal, but the resistance passes through a minimum, and above a pressure varying with temperature from 8000 to 10000, increases again. This is the behavior of Cs, which occupies the adjoining cell in the first column of the periodic table, and is the only other known example.

Measurements were made at 0° , 30° , and 75° , at the latter temperature first. At 75° , there was some chemical action, which resulted in a gradual increase of resistance during application of pressure, amounting in the aggregate to 1.1% of the total resistance. The mean of the results found with increasing and decreasing pressure was taken as the best results to be found from this run; the mean points lay on a smooth curve within the limit of the sensitiveness of the readings, which was about 0.14% of the maximum pressure effect. At 30° , there was no chemical action, and no point lay off a smooth curve by more than 0.2 mm. of the slide wire setting of the potentiometer, the maximum displacement of the slider being 4 cm. At 0° , again there was a small permanent change of resistance of 0.2% of the total resistance, probably not due in this case to chemical action, but to distortion of the wire brought about by the viscosity of the transmitting medium. This is to be expected because barium is a rather soft metal. The mean of the up and down points at 0° did not lie off a smooth curve by more than 0.1 mm. of the slide wire.

The results are contained in Table I. It will be seen, as already stated, that the resistance passes through a minimum, and that the pressure of the minimum is a temperature function. Within experimental error, the relation between temperature and the pressure of the minimum is linear, being 8100 kg. at 0° and 9600 kg. at 75° .

TABLE I.

RELATIVE RESISTANCE OF BARIUM AS A FUNCTION OF PRESSURE AND TEMPERATURE.

Pressure kg./cm ²	Resistance		
	0°	30°	75°
1	1.0000	1.1520	1.4380
1000	.9922	1.1408	1.4183
2000	.9855	1.1319	1.4028
3000	.9803	1.1251	1.3904
4000	.9764	1.1198	1.3805
5000	.9736	1.1156	1.3726
6000	.9717	1.1127	1.3665
7000	.9707	1.1109	1.3613
8000	.9705	1.1100	1.3586
9000	.9710	1.1100	1.3569
10000	.9721	1.1107	1.3565
11000	.9739	1.1123	1.3581
12000	.9764	1.1144	1.3620

In addition to the measurements under pressure, careful measurements were made of the temperature coefficient of resistance at atmospheric pressure. The maximum temperature was limited to 75°, in order to avoid error from chemical action, which however did not prove troublesome after the first exposure to 75°. Temperature was varied in both directions from the mean temperature several times, and the results always lay on a smooth curve. A second degree equation in the temperature will not quite reproduce the results. A third degree curve through the points at 0°, 30°, 50° and 75° has the equation:

$$\frac{\Delta R}{R_0} = .004795t + 5.71 \times 10^{-5}t^2 + 1.119 \times 10^{-6}t^3.$$

The mean coefficient between 0° and 100°, given by extrapolation with this equation, is 0.00649, which is very high, and evidence of high purity.

Thorium. I owe this metal to the kindness of Dr. Rentschler of the Westinghouse Lamp Co. The compressibility sample was in the form of a rod about 3 mm. in diameter, and 2.7 cm. long. It had been prepared in the laboratory of the Westinghouse Co., and was

known to be of high purity, as far as foreign metals are concerned, but the method of preparation did not ensure the absence of all oxides. The resistance sample was in the form of wire, 0.07 cm. in diameter, which was especially prepared for these measurements in the Westinghouse Laboratory, so as to be free from all oxides, as well as metallic impurities. I am much indebted to Dr. Rentschler for the pains which he took in the preparation of this sample.

Compressibility. Runs were made as usual at 30° and 75°. Thorium is known to be cubic. The volume compressibility, calculated from the linear compressibility, is:

$$\text{At } 30^{\circ} \quad \frac{\Delta V}{V_0} = -18.18 \times 10^{-7}p + 12.78 \times 10^{-12}p^2.$$

$$\text{At } 75^{\circ} \quad \frac{\Delta V}{V_0} = -18.46 \times 10^{-7}p + 13.29 \times 10^{-12}p^2.$$

At 30° the average departure of a single reading from a smooth curve was 0.61%, and at 75° 0.31%.

Resistance. The resistance was measured with the potentiometer in the regular way. Connections were made to the thorium wire with small springs, it not being possible to solder it. The results were:

$$\text{At } 30^{\circ} \quad \frac{\Delta R}{R(1 \text{ kg}, 30^{\circ})} = -2.787 \times 10^{-6}p + 1.89 \times 10^{-11}p^2.$$

$$\text{At } 75^{\circ} \quad \frac{\Delta R}{R(1 \text{ kg}, 75^{\circ})} = -2.966 \times 10^{-6}p + 2.18 \times 10^{-11}p^2.$$

The average numerical deviation of a single reading from a smooth curve was 0.07% at 30° and 0.11% at 75°.

At atmospheric pressure the resistance was measured at 20°, 55°, 75°, and 90°. Within this range, resistance varies linearly with temperature. The average temperature coefficient between 0° and 100° is 0.00239 at 0°. This is surprisingly low, considering the presumably high purity of this metal.

Chromium. The only sample available was a massive, strongly crystalline lump of unknown purity, which I owe to the courtesy of the Hoskins Co. of Detroit. This metal was not quite as hard as hardened steel tools, and by sacrificing many hack saw blades, a rod 2.7 cm. long and 6 mm. in diameter was obtained for the compressibility measurements. No attempt was made to measure the

resistance; the probable purity did not justify the effort. Chromium is known to be cubic. The following results were found for the volume compressibility from the measurements of linear compressibility.

$$\text{At } 30^{\circ} \quad \frac{\Delta V}{V_0} = -5.187 \times 10^{-7}p + 2.19 \times 10^{-12}p^2.$$

$$\text{At } 75^{\circ} \quad \frac{\Delta V}{V_0} = -5.310 \times 10^{-7}p + 2.19 \times 10^{-12}p^2.$$

The average numerical deviation of a single reading from a smooth curve was 0.48% at 30°, and 0.93% at 75°.

The compressibility given above for Cr is very much less than that found by Richards,⁹ who gives the value 9×10^{-7} . That there was very great doubt about the value of Richards is indicated by the fact that he gave only one significant figure.

Vanadium. This material I owe to the courtesy of Mr. B. D. Saklatwalla of the Vanadium Corporation of America. It was highly crystalline and brittle, and came in the form of small rectangular prisms bounded by the cleavage faces, so that the specimen was without doubt a single crystal. Since vanadium is cubic, the linear compressibility of a single crystal in a single direction gives the material for calculating the cubic compressibility. The Vanadium Corporation provided a partial analysis of the material. The best sample was described as 95.02% Va, and .07% C; this was the sample on which measurements were made.

The cubic compressibility, calculated from the linear compressibility was:

$$\text{At } 30^{\circ} \quad \frac{\Delta V}{V_0} = -6.090 \times 10^{-7}p + 2.58 \times 10^{-12}p^2.$$

$$\text{At } 75^{\circ} \quad \frac{\Delta V}{V_0} = -6.117 \times 10^{-7}p + 2.55 \times 10^{-12}p^2.$$

The average numerical deviation of a single reading from a smooth curve was 0.11% at 30° and 0.10% at 75°.

No attempt was made to measure the resistance under pressure.

Phosphorus. Measurements were made on both the red and the black modifications.

Red Phosphorus. Although this variety of phosphorus is technically described as "red," violet would more closely describe its appear-

ance. This sample had been formed in 1915 from white phosphorus in the presence of a trace of sodium as a catalyzer by heating to 200° C. under a pressure of 4000 kg, and then increasing the pressure to 12000.¹⁰ The density was 2.348 at room temperature. Since 1915 it has been kept sealed in glass. This specimen possessed no apparent structure. The fracture was conchoidal in character, and extremely fine grained; it probably is a microscopic aggregate of crystals arranged approximately at random. The crystal system of red phosphorus has apparently not yet been determined, but the probability is that it is not cubic. It is to be expected from the manner of formation that the linear compressibility of my sample would be approximately the same in all directions, and that therefore the cubic compressibility could be calculated from a single measurement of linear compressibility. This was checked, however, by making measurements in two different directions. The linear compressibility of a piece 1 cm. long was first measured, and then this piece was cut transversely, and two of the resulting pieces piled together to make a length of 0.5 cm. perpendicular to the original direction, and the linear compressibility of this also measured. The linear compressibilities in these two directions were not the same, but differed by a maximum of 14% at 30° and 12% at 75° , that of the longer single specimen being the greater. This would seem to show that red phosphorus cannot be cubic, and also that in my particular specimen there was a preferred direction of orientation.

The compressibility of neither specimen can be given by a two-power series in the pressure, but the maximum departure from linearity occurs at a pressure less than the mean pressure. This means that the initial rate of decrease of compressibility with increasing pressure is greater than the final rate of decrease. The two samples did not agree, however, with regard to the temperature behavior; the linear compressibility of the longer sample behaved abnormally in that it was less at 75° than at 30° by an amount varying from 4.5% at atmospheric pressure to 1.7% at 12000 kg, whereas that of the shorter sample was less at 30° than at 75° by an amount varying from 1.0% at atmospheric pressure to 5% at 12000. The accuracy of the measurements on the two samples was about the same, the average departure of a single reading from a smooth curve being about 0.3%.

The smoothed average of the results for the two specimens, converted from change of length to change of volume, is shown in Table II.

TABLE II.

VOLUME CHANGE OF RED PHOSPHORUS AS A FUNCTION OF PRESSURE AND TEMPERATURE.

Pressure kg/cm ²	$\Delta V/V_0$	
	30°	75°
2000	.0101	.0100
4000	.0190	.0189
6000	.0270	.0270
8000	.0342	.0344
10000	.0408	.0412
12000	.0469	.0476

The initial compressibility of this red phosphorus may be found by extrapolation to be about 5.45×10^{-6} at 30°. This is very much less than the value given by Richards⁹ for red phosphorus, namely 9.0×10^{-6} . The red phosphorus of Richards was apparently the red phosphorus of commerce. The density of this is much less than the density of my violet phosphorus, so that it is probable that it was in a state of suspended equilibrium, and contained an appreciable proportion of untransformed white phosphorus molecules, which would account for the difference.

Black Phosphorus. This was the identical sample, the pressure coefficient of the resistance of which has been previously measured.¹¹ It has been kept sealed in glass since those measurements. The linear compressibility of this was measured in only a single direction. Black phosphorus is known not to be cubic; the crystal structure of this specimen was microscopically fine, however, and there is no doubt from the appearance of the specimen that all orientations contributed to the final result. The example of red phosphorus shows, however, that there may nevertheless be a preferred direction, so that the cubic compressibility can be calculated from the linear compressibility only with considerable uncertainty. For this reason I give in the following (Table III) only two significant figures for the initial cubic compressibility, calculated on the assumption of equal compressibility in all directions. The average deviation of a single reading from a smooth curve was 1.0% at 30°, and 1.1% at 75°.

The absolute compressibility is seen to be about one-half that of red phosphorus. The variation of compressibility with temperature is similar to that of red phosphorus, in that the temperature coefficient

TABLE III.

VOLUME CHANGE OF BLACK PHOSPHORUS AS A FUNCTION OF PRESSURE AND TEMPERATURE.

Pressure kg/cm ²	$\Delta V/V_0$	
	30°	75°
2000	.0052	.0052
4000	.0095	.0095
6000	.0129	.0129
8000	.0158	.0158
10000	.0182	.0185
12000	.0205	.0209

does not assume an appreciable positive value until the highest pressures are reached. There is, however, a striking difference between the effect of pressure on the compressibility of red and black phosphorus. The compressibility of red phosphorus at 30° drops from 5.45×10^{-6} at atmospheric pressure to 0.54 of this value at 12000 kg., whereas the compressibility of black phosphorus at 30° drops from 2.9×10^{-6} at atmospheric pressure to 0.38 of this at 12000. That is, the relative drop in the compressibility of black phosphorus is greater in spite of the fact that its absolute compressibility is much less. This is not usual, and is directly opposed to a rule proposed by Professor Richards.¹² It would seem to indicate that structural differences in the intermolecular spaces furnish a comparatively greater contribution to the initial compressibility of black phosphorus, and that the compressibility of the *molecule* of black phosphorus is appreciably less than even one-half that of the molecule of red phosphorus.

Sulfur. Sulfur is not cubic, but orthorhombic, so that a complete description of the change of dimensions under pressure demands a measurement of the linear compressibility in the three crystallographically independent directions. Fortunately sulfur occurs in nature in large clear crystals, so that the material is comparatively easy to obtain. I am indebted to the Harvard University Museum for the single crystals of my measurements. Great care is needed in cutting the specimens, because of the great brittleness of this substance and its extreme sensitiveness to temperature changes, the heat of the hand being sufficient to crack it. The method finally adopted was to whittle the specimen with a razor blade from a large

crystal, which was imbedded in plaster of paris. Care must be taken that the plaster is of the same temperature as the crystal before imbedding.

A special form of holder had to be used, because sulfur is soluble in the kerosene or petroleum-ether by which pressure is transmitted. A holder was designed which permitted the sulfur to be submerged beneath a surrounding mass of water, pressure being transmitted to the water by oil as usual. A further difficulty was that under pressure the sulfur attacks the steel of the holder, forming ferrous sulfate. This action was reduced to a harmless amount by gold plating the holder, a suggestion for which I am indebted to my assistant Mr. W. N. Tuttle. Since the compressibility of steel and gold are almost exactly the same, no error is introduced by the plating.

Measurements were made of the linear compressibility in three directions at 30° and 75°, in the regular way. The designation of these directions is that conventional with crystallographers. The "a" and "b" directions are in the plane of the rhombic table-like faces. "a" bisects the acute angle, and "b" the obtuse angle. The "c" direction is perpendicular to "a" and "b".

In no case could the results be represented by a two-power series in the pressure, but the compressibility drops initially faster than given by such a relation. The results are collected in Table IV,

TABLE IV.
THE COMPRESSIBILITY OF RHOMBIC SULFUR.

Pressure kg/cm ²	$\Delta l/l_0$						$\Delta V/V_0$	
	Direction "a"		Direction "b"		Direction "c"			
	30°	75°	30°	75°	30°	75°	30°	75°
2000	.0099	.0104	.0093	.0113	.0042	.0043	.0233	.0258
4000	.0180	.0190	.0165	.0201	.0079	.0082	.0419	.0466
6000	.0246	.0261	.0224	.0273	.0113	.0116	.0571	.0638
8000	.0304	.0323	.0277	.0334	.0143	.0148	.0707	.0784
10000	.0357	.0372	.0323	.0388	.0171	.0177	.0839	.0908
12000	.0412	.0427	.0370	.0433	.0198	.0203	.0949	.1027

giving the change of linear dimensions at intervals of 2000 kg., and also the change of volume, calculated from the change of linear dimensions. The accuracy is indicated by the average departure of a single reading from a smooth curve, and was as follows: direction "a", at 30°, 0.47% deviation, and at 75°, 0.67% deviation; direction

"b", at 30°, 0.69% deviation, and at 75°, 0.63% deviation; direction "c", at 30°, 1.42% deviation, and at 75°, 0.55% deviation.

The initial compressibility, which may be found by extrapolation of the above values, is 13.2×10^{-6} at 30° and 14.4×10^{-6} at 75°. This gives 12.9×10^{-6} at 20° for the initial compressibility, or 12.7×10^{-6} as the average compressibility between 100 and 500 kg, at 20°. This latter agrees exactly with the value found by Richards.⁹

Discussion and Survey.

Most of these new results on compressibility can be dismissed with little further discussion. It will be found that the compressibilities fall entirely into line with what would be expected from the position of the metals in the periodic table. A convenient way to exhibit the relationship is to plot the logarithm of the compressibility to the base 10 against atomic number. This is shown in Figure 1.

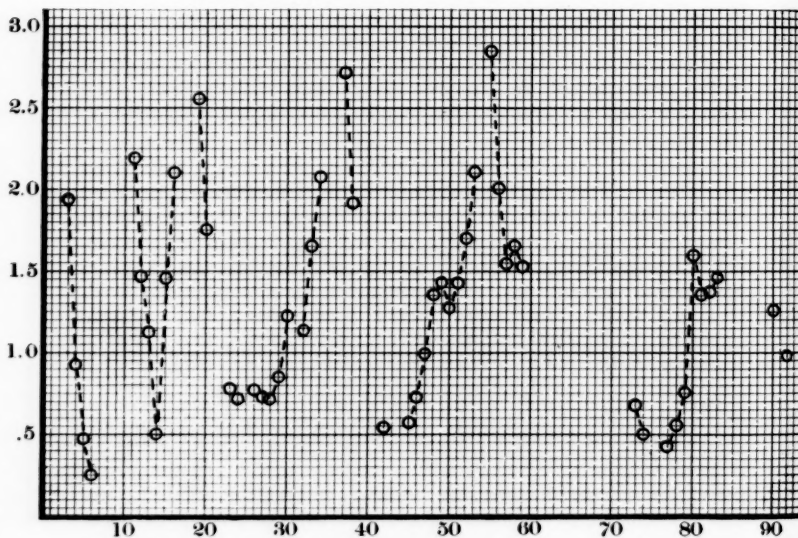


FIGURE 1. The logarithm to the base 10, plus 7, of the compressibility plotted as ordinate against the atomic number as abscissa.

Va and Cr come about where they would be expected, being nearly the same as Fe, Co, and Ni. A good value for manganese is needed to complete our knowledge of this portion of the periodic table; it is evident that there is some sort of minor irregularity in this group of elements. The compressibility of Be falls smoothly between that of Li on the one side, and that of *B* and *C* (diamond) on the other. Apparently black *P* must be considered the normal modification of *P*, since its compressibility falls more smoothly between that of Si and *S* than does that of the red modification, whereas the compressibility of white *P* falls entirely out of sequence. The compressibility of Ba falls smoothly between that of Cs and La, and also terminates the increasing sequence Ca, Sr, Ba, as would be expected. The compressibility of Th is very materially higher than that of Ur, but no other elements have been measured in this part of the table, so we cannot tell whether this was what was to be expected or not. The group of three elements, La, Ce, Pr, (atomic numbers 57, 58, and 59) perhaps offers the most unexpected feature shown by these ten elements, the compressibility of Ce being higher than that of either La or Pr, although the general situation on the falling branch of the curve would lead to the expectation of an intermediate value. But we have seen that the compressibility of Ce is by itself highly anomalous, the temperature coefficient being negative, and the curvature in the abnormal direction. Doubtless there is some connection with the new polymorphic form stable at high pressures.

The phenomena of electrical resistance under pressure are much less simple than those of compressibility. These new data only increase the sense of confusion in this domain that has been increasing with every further penetration into unusual parts of the periodic table. When I began my measurements on the effect of pressure on resistance, the facts seemed very simple, for the resistance of every known element decreased under pressure with the single exception of Bi, and this element is exceptional in so many of its properties that an exception in the pressure coefficient of resistance was more to be expected than not. But the list of elements whose resistance increases under pressure has rapidly grown to: Bi (solid only), Sb, Li (both liquid and solid), Ca, Sr, Ti (perhaps), Cs at high pressure, and now Ce (low pressure modification), and Ba (at high pressures).

The similar behavior of Cs and Ba is striking and perhaps significant, but that we cannot yet put our fingers on the precise feature which is responsible for the similarity is shown by the diametrically opposite behavior of the three pairs of elements above Cs and Ba in the periodic table, namely, Li and Be, K and Ca, and Rb and Sr.

It is interesting that in the group of four successive elements in the table, Cs, Ba, La, and Ce (numbers 55, 56, 57, and 58), three are highly anomalous, Cs and Ba being the only elements found thus far with a pressure minimum of resistance, and Ce having two modifications, of which the low pressure modification is highly anomalous in several respects, as we have seen. Why is it that La is entirely normal, as is also Pr, the next element, of atomic number 59?

The behavior of these new elements only strengthens the view to which I have been coming for some time, namely that the mechanism of electrical conductivity is not as simple as at first appeared, but that a single type of mechanism is not competent to explain the various behavior of different metals.

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